

LABORATORY BATCH TEST EVALUATION OF FIVE FILTER MATERIALS FOR REMOVAL OF NUTRIENTS AND PESTICIDES FROM DRAINAGE WATERS

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ABSTRACT. Where subsurface drainage practices are employed, fertilizer nutrients and pesticides applied on farm fields and municipal locations are commonly intercepted by the buried drainage pipes and then discharged into local streams and lakes, oftentimes producing adverse environmental impacts on these surface water bodies. Various filter materials have the potential to remove nutrient and pesticide contaminants from subsurface drainage waters before these waters are released offsite. For this study, laboratory batch tests were conducted to evaluate the contaminant removal effectiveness and efficiency of five potential filter materials. The five materials, isolated from previous screening tests, were steam activated carbon, high calcium oxide-high carbon fly ash, iron sulfide, sulfur-modified iron, and surfactant-modified zeolite. Filter material effectiveness was tested against initial contaminant solution concentrations that varied between 10 and 200 mg L⁻¹ for nitrate-N, 0.1 and 1.0 mg L⁻¹ for phosphate-P, and 0.1 and 0.5 mg L⁻¹ for atrazine, while filter material efficiency was evaluated with respect to exposure time by varying test durations from 1 to 24 h. Sulfur-modified iron proved best for treating nitrate, based on reductions greater than 95% across the range of initial concentration levels and exposure times. Surfactant-modified zeolite and high calcium oxide-high carbon fly ash affected the greatest removal of phosphate, 50% or more in all cases. For atrazine, the most promising results were obtained with steam activated carbon and high calcium oxide-high carbon fly ash, which removed almost 100% of this particular pesticide regardless of initial concentration level and exposure time. Consequently, there are several filter materials, when used either alone or in combination, that show promise for removing mixed contaminants from subsurface drainage water; however, more laboratory testing followed by field experiments are needed to completely evaluate their feasibility for widespread use.

Keywords. Atrazine, Batch tests, Filter materials, Nitrate, Phosphate, Subsurface drainage, Water quality.

Agricultural fertilizer and pesticide application combined with subsurface drainage practices have produced adverse water quality impacts within the U.S. on local, regional, and national scales. One prime example is the Midwest and Northeast U.S. portion of lands draining into Lake Erie or Lake Saint Clair. These lands are 75% agricultural, with substantial corn, soybean, and wheat production. As a result of intense farming operations and the use of subsurface drainage, the streams within this area have some of the highest levels of fertilizer-derived nutrients (nitrate and total phosphorus) and pesticides found in streams nationally (Myers et al., 2000). For another example, nitrogen and phosphorus nutrients from agricultural fertilizer application have been determined to be largely responsible for the hypoxic zone in the Gulf of Mexico (Sylvan et al., 2006; Scavia and Donnelly, 2007); the Midwest U.S., where subsurface drainage systems are

widespread, is a primary source of these nutrients (Goolsby and Battaglin, 2000; Alexander et al., 2008).

Subsurface drainage, a common farm practice in cool, humid climates of Canada, parts of Europe, and the Midwest U.S., is used to remove excess soil moisture by lowering shallow water table levels, thereby improving crop yields (Beauchamp, 1987; Pavelis, 1987; Smedema et al., 2004). Subsurface drainage is also employed on irrigated farmland within arid and semiarid climate regions (e.g., parts of California and Australia) to improve crop production by preventing waterlogged soil conditions and soil salinity buildup (Smedema et al., 2004). Although subsurface drainage systems (comprised of buried drainage pipe networks) certainly provide substantial economic benefit, they also have adverse environmental consequences because nutrients (nitrate-phosphate) and pesticides are often intercepted by the buried drainage pipes and then discharged directly into local waterways (Zucker and Brown, 1998). In order to mitigate the adverse environmental impacts of subsurface drainage, various on-site water treatment options need to be considered, evaluated, and implemented.

Nitrate (NO₃⁻) is often regarded as the major environmental concern with respect to subsurface drainage. Research conducted in the Midwest U.S. and Canada indicates that the nitrate-nitrogen (NO₃⁻-N) concentration in waters discharged from agricultural subsurface drainage systems typically ranges from 0 to 50 mg L⁻¹, although higher values are certainly possible (Zucker and Brown, 1998;

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Kalita et al., 2006; Kalita et al., 2007). The amount of NO_3^- in agricultural subsurface drainage waters depends on a number of factors, including soil conditions, farm operations, time of year, subsurface drainage system characteristics, water table management strategies, etc. (Drury et al., 1996; Kladvko et al., 2004; Kanwar et al., 2005; Jaynes and Colvin, 2006; Bakhsh and Kanwar, 2007; Oquist et al., 2007). Studies indicate that significant amounts of NO_3^- can also leach through the soil profile in areas covered by turfgrass. The magnitude of the resulting environmental hazard depends on factors such as type of fertilizer applied, timing of fertilizer application, irrigation volume, irrigation timing, soil conditions, etc. (Petrovic, 1990; Guillard and Kopp, 2004). Consequently, given the proper situation, municipal locations like golf courses or commercial/residential areas that contain subsurface drainage systems may pose a potential risk for NO_3^- release into local waterways.

Phosphate (PO_4^{3-}), as previously indicated, is another nutrient typically found in subsurface drainage waters. Kladvko et al. (1991) measured agricultural subsurface drainage phosphate-phosphorus ($\text{PO}_4^{3-}\text{-P}$) values in the range of 0.005 to 0.1 mg L^{-1} at an experimental field site in Indiana. Laubel et al. (1999) monitored storm event $\text{PO}_4^{3-}\text{-P}$ in the range of 0.04 to 0.39 mg L^{-1} at the subsurface drainage pipe network outlet for a small agricultural watershed in Denmark. Phosphate can also be discharged from subsurface drainage systems in municipal settings. Median $\text{PO}_4^{3-}\text{-P}$ values of 0.09 and 0.11 mg L^{-1} were measured by King et al. (2006) at two sites on a golf course located in Austin, Texas. Consequently, based on past investigations, subsurface drainage $\text{PO}_4^{3-}\text{-P}$ values above 0.5 mg L^{-1} , particularly in agricultural settings, would be considered fairly unusual (Sims et al., 1998; Kinley et al., 2007).

Pesticides, as already pointed out, are often present in agricultural drainage water (Kladvko et al., 1991; Dousset et al., 2004), and atrazine happens to be one of the most common. Atrazine is generally found in subsurface drainage waters at relatively low concentrations, usually well below 0.1 mg L^{-1} (Gaynor et al., 1995a; Kladvko et al., 1999; Yuan et al., 2000). However, Gaynor et al. (1995b) measured a maximum subsurface drainage water atrazine concentration of 0.35 mg L^{-1} in research conducted on small test plots. Therefore, high atrazine concentrations in agricultural subsurface drainage waters are possible.

Controlled drainage practices (Frankenberger et al., 2007), wetland water treatment (Kovacic et al., 2000; Tanner et al., 2005), and bioreactors (Blowes et al., 1994) have all been evaluated for their potential to remove contaminants from subsurface drainage waters, and each of these three methods has its advantages and disadvantages. In-line filter systems installed at some location along the pipe outlet of a subsurface drainage system are another alternative for treating drainage waters before these waters are discharged into local waterways. Filter trenches, bottom-lined with impermeable material (clay or geomembranes) to prevent leaching, can be placed in-line on the pipe outlet to treat subsurface drainage waters in larger-scale settings such as agricultural fields. However, for smaller-scale subsurface drainage pipe networks, such as those found at golf courses or in commercial/residential areas, reduced-size flow-through filter cells or filter cartridges installed in-line on the pipe outlet might be a better choice for cleaning drainage water.

Based on prior permeable reactive barrier research (Tratnyek et al., 1997; Bowman, 2003; Leglize et al., 2006), activated carbon, zero-valent iron, and surfactant-modified zeolite are three of the more promising filter materials potentially applicable for treatment of mixed nutrient and pesticide contaminants present in subsurface drainage waters. For activated carbon, most of the surface area is nonpolar. As such, when an activated carbon filter is partially or fully saturated with an aqueous solution, organic solutes (e.g., pesticides like atrazine) originally present in solution can become adsorbed onto the nonpolar activated carbon surfaces via London and van der Waals dispersion forces and hydrophobic interactions (Rosen, 1989; McBride, 1994). However, activated carbons also have some charged, pH-dependent, oxygen-containing functional groups on particle surfaces (Rivera-Utrilla and Sanchez-Polo, 2002; Tsang et al., 2007). If the pH of the saturated/unsaturated activated carbon filter material environment is less than the activated carbon point of zero charge (PZC), then negatively charged solutes (e.g., NO_3^-) can potentially become electrostatically adsorbed at these surface functional group sites (Sparks, 2003). Activated carbon PZC has been found to range from 2.9 to 9.7 (Rivera-Utrilla and Sanchez-Polo, 2002; Giraldo and Moreno-Pirajan, 2007; Liu et al., 2008; Srivastava et al., 2008). Removal of PO_4^{3-} by activated carbon would probably involve ligand exchange at certain oxygen-containing functional group sites, where PO_4^{3-} anions become incorporated into the surface chemical structure of a substrate (Bohn et al., 1985; McBride, 1994).

Zero-valent iron filter materials have a demonstrated capability for removing a wide variety of organic and inorganic contaminants from water (Benner et al., 1997; Tratnyek et al., 1997; Ghauch et al., 1999; Dombek et al., 2004; Dries et al., 2005). In particular, zero-valent iron degrades nitrate (NO_3^-) to nitrogen gas (N_2) and ammonium ions (NH_4^+) by means of both biological and abiotic NO_3^- electrochemical reduction (Biswas and Bose, 2005). Iron oxide/hydroxide formation on zero-valent iron particle surfaces can provide sites for PO_4^{3-} removal via ligand exchange (Huang et al., 2003; Tyrovola et al., 2006). Chloro-organic pesticides, such as atrazine, are degraded by zero-valent iron via reductive dechlorination (Ghauch et al., 1999; Dombek et al., 2001; Dombek et al., 2004).

Surfactant-modified zeolite is another filter material potentially capable of removing oxyanions (NO_3^- , PO_4^{3-} , etc.) and pesticides from subsurface drainage waters. Zeolites are hydrous aluminosilicate minerals with high external and internal surface areas, along with a large cation exchange capacity. Under typical conditions, zeolite particle surfaces have substantial net negative charge. However, treatment of zeolite with a solution containing a sufficient amount of the proper cationic surfactant results in the formation of surfactant bilayers on external zeolite surfaces, as illustrated in figure 1 (Sullivan et al., 1997; Bowman, 2003). In a surfactant-modified zeolite porous medium partially or completely saturated by an aqueous solution, surface charge reversals, from negative to positive, occur where surfactant bilayers form (fig. 1), with the surfactant/water interface at these bilayer locations now a potential site for electrostatic adsorption of anions, such as NO_3^- and PO_4^{3-} (Bowman, 2003). The interlayer of the surfactant bilayer is comprised of the hydrophobic hydrocarbon chain portions of the surfactant molecules (fig. 1) and, as such, provides a

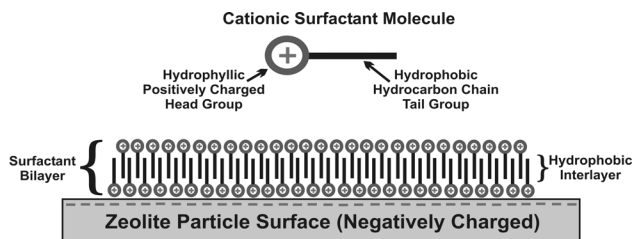


Figure 1. Schematic of surfactant bilayer covering zeolite particle surface.

medium in which nonpolar organic compounds can be partitioned out of the aqueous solution via hydrophobic interactions (Bowman, 2003). Some chloro-organic pesticides, such as atrazine, are moderately polar (Xing et al., 1996), so while it is more likely for these moderately polar organic compounds to become incorporated into the hydrophobic interlayer of the surfactant bilayer, it may also be possible that these compounds are adsorbed at internal negatively charged mineral/water interfaces (Bowman et al., 1995) or external positively charged surfactant/water interfaces.

Preliminary batch test screening results (unpublished) for 60 industrial products/byproducts isolated five different materials having the greatest promise for removing mixed nutrient (NO_3^- and PO_4^{3-}) and pesticide (atrazine) contaminants from subsurface drainage waters. These five most promising filter materials were a steam activated carbon, a high calcium oxide-high carbon fly ash, an iron sulfide (FeS), a sulfur-modified iron, and a cationic surfactant-modified zeolite. Interestingly, these preliminary screening tests showed that the high iron content products, iron sulfide and sulfur-modified iron, were much better at removing NO_3^- than zero-valent iron, even though the NO_3^- removal mechanism for iron sulfide and sulfur-modified iron were likely the same as the NO_3^- removal mechanism for zero-valent iron. Sulfur-modified iron, which is not well known and has not been extensively tested for water treatment, is a hydrogen-reduced, high surface area iron powder (zero-valent iron) that has been additionally modified through chemical reaction with pure sulfur to produce a sulfur/iron compound(s) surface coating on the iron particles. None of the five filter materials mentioned have been extensively tested for subsurface drainage water treatment. Consequently, this study focused on additional laboratory batch testing of these five filter materials to further evaluate their nutrient/pesticide removal effectiveness and efficiency. The overall research goal was to document the filter materials that alone or in combination have potential to effectively and efficiently remove mixed nutrient and pesticide contaminants from subsurface drainage waters. The guiding hypothesis for this research can therefore be stated as: “At least one of the filter materials tested will exhibit potential to effectively and efficiently remove NO_3^- from drainage waters, at least one will be potentially effective/efficient for removing PO_4^{3-} , and at least one will be potentially effective/efficient for removing atrazine.”

MATERIALS AND METHODS

FILTER MATERIALS

The five filter materials evaluated in this investigation, including the notation used for their designation throughout the rest of this article, are as follows:

- AC = steam activated carbon, 0.8 mm pellets, source: Alfa Aesar (Ward Hill, Mass.). The parent material for this activated carbon is unknown.
- FA = high calcium oxide (18%) and high carbon (20%) fly ash, source: Mintek Resources (Beavercreek, Ohio).
- IS = iron(II) sulfide, chemical formula: FeS, source: Alfa Aesar (Ward Hill, Mass.).
- SMIr = sulfur-modified iron, developer/marketer: SMI_PS, Inc. (Walnut Creek, Cal.), producer: North American Hoganas, Inc. (Hollsopple, Pa.). A general description of sulfur-modified iron is provided in the last paragraph of the preceding section.
- SMZeo = surfactant-modified zeolite. Surfactant is Maquat NKC-50 I (alkyldimethylnaphthyl ammonium chloride solution) obtained from Mason Chemical Co. (Arlington Heights, Ill.), zeolite is clinoptilolite obtained from Z-olite, Inc. (Smithfield, Utah).

Because they were initially in a dry granular form, there was no preparation required for AC, FA, IS, and SMIr.

Maquat NKC-50 I, which was used for preparing SMZeo, is a liquid containing 50% cationic surfactant active ingredient, 40% water, and 10% isopropanol. The cationic surfactant active ingredient is alkyldimethylnaphthyl ammonium chloride (ADMNA). On the molecular level, this recently developed cationic surfactant has a chemical structure comprised of a linear alkyl chain connected to dimethyl ammonium group, which is then linked via an isolated carbon atom to a naphthyl group. Hexadecyltrimethyl ammonium bromide/chloride (HDTMA) is the cationic surfactant most commonly used to produce surfactant-modified zeolite materials that are being tested and employed for water treatment (Bowman et al., 1995; Campos and Buchler, 2007; Cortes-Martinez et al., 2009; Yusof and Malek, 2009). However, the cationic surfactant utilized in this study, ADMNA, was chosen over HDTMA because, in prior laboratory screening batch tests, ADMNA-modified zeolite performed better than HDTMA-modified zeolite for removing nutrient/pesticide contaminants from water. The SMZeo filter material itself was generated by mixing 100 g of Maquat NKC-50 I solution, 250 g of zeolite, and 500 g distilled water. This mixture of surfactant/zeolite/water was allowed to equilibrate for 24 h before liquid was drained off, and the SMZeo granular material was then placed in a sealed plastic storage bag. The remaining water present within the SMZeo was 19.4% by weight, as determined by oven drying at 105°C.

Filter material properties are provided in table 1. The values for pH, electrical conductivity (EC), and oxidation/reduction potential (ORP) were obtained from a slurry mixed for 1 h that contained 10 g of de-ionized water and 5 g of filter material. The equipment employed to measure pH, EC, and ORP are listed in the Experimental Procedures subsection. A set of different-sized sieves (#4, #10, #20, #40, #60, #100, #140, and #200) was used to determine the particle size

Table 1. Filter material properties.

Filter Material	pH ^[a]	EC ^{[a],[b]} (dS m ⁻¹)	ORP ^{[a],[c]} (mV)	Particle Size Distribution ^[d] (%)		
				Coarse/Medium Sand (4.76 to 0.42 mm)	Fine Sand (0.42 to 0.075 mm)	Silt and Clay (<0.075 mm)
AC	8.15	6.24	142	99.60	0.28	0.12
FA	11.48	6.86	-231	0.14	43.31	56.55
IS	5.88	4.11	-444	19.29	49.58	31.13
SMIr	6.65	6.79	-664	15.22	78.40	6.38
SMZeo	6.74	0.55	48	94.9	4.95	0.15

[a] Measurements obtained from 1 to 2 by weight mixtures of filter material to de-ionized water.

[b] Electrical conductivity (EC) of solution measured in decisiemens per meter (dS m⁻¹).

[c] Oxidation/reduction potential (ORP) of solution measured in millivolts (mV).

[d] A set of different-sized sieves (#4, #10, #20, #40, #60, #100, #140, and #200) was used to determine the particle size distribution.

distribution. The pH values for AC, IS, SMIr, and SMZeo range from slightly acidic to slightly alkaline, while FA is highly alkaline. Electrical conductivity values for AC, FA, IS, and SMIr were relatively high (4 to 7 dS m⁻¹), while EC for SMZeo was quite small (<1 dS m⁻¹). The ORP results in table 1 indicate that low redox conditions potentially conducive to nitrate electrochemical reduction to ammonia/ammonium or nitrogen gas are likely to exist in a saturated filter packed with FA, IS, or SMIr. There are noteworthy differences in particle size distribution between the five materials tested in this study. The AC and SMZeo filter materials have a particle size similar to that of a coarse/medium sand. Silt and clay sized particles comprise well over half the FA material. The IS material has a wide mixture of particle sizes, with significant amounts of coarse/medium sand (~20%), fine sand (~50%), and silt/clay particle sizes (~30%). The SMIr filter material has a particle size predominantly similar to fine sand. Although not measured, all five filter materials are likely to have significant internal porosity within particles.

NITRATE/PHOSPHATE/ATRAZINE SOLUTIONS

The five filter materials were tested against three solutions containing moderate, high, and extreme concentration levels of nitrate (NO₃⁻), phosphate (PO₄³⁻), and atrazine. These solutions were designated as having moderate, high, and extreme concentrations of contaminants based on prior literature documenting NO₃⁻, PO₄³⁻, and atrazine levels in subsurface drainage waters. The constituents present in the three solutions are listed in table 2. The 565 mg L⁻¹ of calcium sulfate (CaSO₄) and 140 mg L⁻¹ of potassium chloride (KCl) were added so that inorganic anions/cations (SO₄²⁻, Cl⁻, Ca²⁺, and K⁺) normally found in drainage water were included in the batch test solutions. When the Na₂HPO₄ added to the test solutions dissolved, a small amount of sodium (Na⁺), another cation commonly found in drainage waters, was introduced along with the PO₄³⁻.

The electrical conductivity (EC) of a solution is used to gauge the solution salinity, and hence the amount of dissolved anions/cations present. The EC measured shortly after mixing was 1.04 dS m⁻¹ for the moderate-concentration

solution, 1.38 dS m⁻¹ for the high-concentration solution, and 2.91 dS m⁻¹ for the extreme-concentration solution. Allred et al. (2008) found an EC range of 1.29 to 3.28 dS m⁻¹ for soil solution extracted by suction lysimeters installed at three northwest Ohio fields having subsurface drainage and clay-textured soils. These field-measured soil solution EC values (1.29 to 3.28 dS m⁻¹), which are similar to the EC values of the test solutions used in this study (1.04 to 2.91 dS m⁻¹), probably represent the upper range of EC values for subsurface drainage under Midwest U.S. conditions. For some added perspective, agricultural subsurface drainage EC values can be substantially larger in locations with arid or semi-arid climates. Subsurface drainage discharge EC values of 32 dS m⁻¹ have been reported for the Murrumbidgee irrigation area of New South Wales, Australia (Hornbuckle et al., 2007), and subsurface drainage EC values as high as 8 dS m⁻¹ (converted from total dissolved solid concentrations) have been measured at the Broadview water district in the San Joaquin Valley, California (Wichelns et al., 2002). With respect to the test solutions utilized for this investigation, based on the most commonly employed salinity classification scale for water extracted from a saturated soil paste (Smedema et al., 2004; Henschke and Hermann, 2007), the moderate- and high-concentration solutions are classified as non-saline (0 to 2 dS m⁻¹), while the extreme-concentration solution is in the slightly saline class (2 to 4 dS m⁻¹). Consequently, the total amounts of dissolved anions and cations present in the research test solutions are not unrealistic considering the wide range of EC measured salinity found around the world for subsurface drainage discharge.

EXPERIMENTAL PROCEDURES

One primary research goal was documenting the contaminant removal effectiveness of the filter materials. Effectiveness, in the context of this investigation, focused only on the percent of the original contaminant removed (or the concentration reduction), given a constant exposure time between the nutrient/pesticide solution and filter material. Because it is possible that contaminant removal effectiveness can be influenced by the contaminant amounts originally present, the filter materials needed to be tested against solutions with different initial concentrations of nutrients and pesticides. Therefore, the first goal of effectiveness assessment was accomplished by measuring NO₃⁻, PO₄³⁻, and atrazine removal amounts from the moderate, high, and extreme concentration solutions based on 4 h duration batch tests.

Table 2. Constituents present in the solutions tested (all values in mg L⁻¹).

Solution Concentration	Nitrate-N (as KNO ₃)	Phosphate-P (as Na ₂ HPO ₄)	Atrazine	CaSO ₄	KCl
Moderate	10 (35)	0.1 (0.46)	0.1	565	140
High	50 (360)	0.25 (1.15)	0.4	565	140
Extreme	200 (1440)	1.0 (4.60)	0.5	565	140

The second primary research goal was evaluation of filter material efficiency in regard to the exposure time needed to remove significant quantities of NO_3^- , PO_4^{3-} , and atrazine contaminants. Filter material efficiency with respect to contaminant removal from solution depends on the rate of the chemical reaction that occurs between the filter material and the contaminant. Questions that are answered by the efficiency assessment include, "Is the amount of contaminant removed from solution by the filter material time dependent?" and perhaps more importantly, "Can a significant amount of contaminant be removed by the filter material in a short period of time?" The overall goal of efficiency assessment was accomplished by measuring the amount of NO_3^- , PO_4^{3-} , and atrazine removed during 24, 4, and 1 h duration batch tests carried out with the high-concentration solution. The 1 h exposure time was the shortest that could be feasibly accommodated with the batch test procedures employed in this study. The 24 h test duration was chosen because a longer exposure time would be unlikely based on rough estimates of the largest practical size for a filter treatment system that could actually be installed in a field setting.

Repeatability of results for nitrate/phosphate/atrazine removal and solution EC was confirmed by conducting a set of six batch test replicates for each filter material, test solution, and test duration combination. A seventh replicate batch test was carried out for each filter material, test solution, and test duration combination in order to measure the pH and oxidation/reduction potential (ORP) within the reaction vessel immediately after batch test completion. The separation process used for the first six replicates, whereby filter material is removed from contact with solution, was found to significantly alter solution pH and ORP. Therefore, the pH and ORP values obtained with the seventh replicated batch test were more representative of actual filter material affected pH and ORP conditions within the Teflon centrifuge tube reaction vessel during batch testing than would be the case for pH and ORP measurements on the separated solution samples obtained from the first six replicates. For baseline comparison purposes, three control sets of six replicate 4 h batch tests were conducted for each of the three solutions (moderate, high, and extreme) without filter material added. One six-replicate control set of batch tests without filter material added was also carried out with the high-concentration solution and a 24 h test duration. Nitrate, phosphate, atrazine, pH, EC, and ORP were measured on the solution samples collected from all control batch test replicates.

In each filter material batch test, with the exception of those conducted with AC, 5 g of filter material and 40 g of solution were combined in a 50 mL Teflon FEP (fluorinated ethylene propylene) centrifuge tube. With the AC batch tests, the difference was that only 38 g of solution could be added to the Teflon centrifuge tube due to the volume occupied by 5 g of AC. The filter material and solution were thoroughly mixed by placing the centrifuge tube containing filter material and solution on a laboratory rotator (Mini LabRoller rotator, Labnet International, Inc., Woodbridge, N.J.) operated at 20 rpm. Each batch was then stopped after a specified period of mixing (24, 4, or 1 h). Procedures for the control batch tests were the same, except of course only solution (40 g), but no filter material, was added to the Teflon centrifuge tube. For those filter material batch tests used to

determine pH and ORP conditions, the pH and ORP measurements were obtained immediately after test completion and directly from the Teflon centrifuge tube reaction vessel containing the filter material and solution mixture. The large majority of batch tests were not used for pH or ORP determinations, and once these tests were completed, the Teflon centrifuge tubes containing filter material and solution were centrifuged at 2500 rpm (800 g) for 10 min in order to separate the filter material from the solution. Part of the solution, set aside for analysis of atrazine, was decanted into a 15 mL glass centrifuge tube and centrifuged at 2500 rpm (800 g) for an additional 60 min and then decanted once more into a second 15 mL glass centrifuge tube to ensure that all filter material had been removed from contact with the solution. The remaining solution in the original Teflon centrifuge tube was used for electrical conductivity (EC) measurement and, most importantly, analysis of NO_3^- and PO_4^{3-} . This remaining solution was itself decanted into a 50 mL polypropylene centrifuge tube and centrifuged at 2500 rpm (800 g) for an additional 60 min and then decanted once more into a 40 mL glass vial, again to ensure that all filter material had been removed from contact with solution. This rather rigorous process of separating the solution from the filter material was done for the purpose of discontinuing chemical reactions between the filter material and test solution after the batch test had finished. For consistency purposes, the same solution separation procedures were employed after completion of the control batch tests, even though these batch tests were conducted with solution only and no filter material.

Solution pH, electrical conductivity (EC), and oxidation/reduction potential (ORP) were measured after completion of each batch test. The solution pH was determined using a Checker pH meter (Hanna Instruments, Woonsocket, R.I.). Solution EC was obtained in decisiemens per meter (dS m^{-1}) with a Field Scout soil and water EC meter (Spectrum Technologies, Inc., Plainfield, Ill.). Solution ORP was measured in millivolts (mV) with an EcoSense pH100 meter and a 115-1 ORP probe (YSI, Inc., Yellow Springs, Ohio). Solution NO_3^- and PO_4^{3-} levels were measured at batch test completion as nitrate-nitrogen (NO_3^- -N) and phosphate-phosphorus (PO_4^{3-} -P), respectively. Nitrate-nitrogen was determined colorimetrically by a copperized-cadmium reduction method (Parsons et al., 1984) using a QuikChem 8000 flow injection analysis system (Lachat Instruments, Milwaukee, Wisc.). Phosphate-phosphorus was determined colorimetrically by an ascorbic acid reduction method (Parsons et al., 1984) also using the QuikChem 8000. Two different methods were employed to measure the atrazine present in solution at batch test completion. Immunoassay (Herzog, 1997) was one of the atrazine analysis methods, and for this method, a RaPID assay atrazine test kit and an RPA-I analyzer (spectrophotometer) were utilized (Strategic Diagnostic, Inc., Newark, Del.). U.S. Environmental Protection Agency Method 525.2, based on gas chromatography-mass spectrometry (GC-MS), was the second atrazine analysis method (Munch, 1995). The GC-MS atrazine analysis done for this study used a Saturn 2200 ion trap GC/MS system (Varian, Inc., Palo Alto, Cal.).

A small number of solution samples from the filter material screening batch tests was submitted for atrazine analysis to an accredited/certified outside laboratory (Soil, Water, and Agricultural Testing Laboratory, New Mexico

State University, Las Cruces, N.M.) for the purpose of evaluating the atrazine analysis accuracy of the immunoassay and GC-MS methods that were used in-house. The outside laboratory atrazine analysis (GC-MS methods) indicated that the in-house immunoassay atrazine analysis tended to be somewhat conservative with respect to the measured filter material induced atrazine removal (higher measured values for atrazine concentration), while the in-house GC-MS atrazine analysis tended to be somewhat optimistic with regard to filter material induced atrazine removal (lower measured values for atrazine concentration). Therefore, in order to avoid bias, results are reported for both the in-house immunoassay atrazine analysis and the in-house GC-MS atrazine analysis.

Because SMIr proved to be the best filter material for removing NO_3^- , two additional batch test sets, each with six replicates, were conducted with SMIr for the purpose of gaining insight into the process by which SMIr removes NO_3^- . All batch tests for these two additional sets were conducted with 50 mL of the extreme-concentration solution mixed with 5 g of SMIr in a polypropylene centrifuge tube over a period of 24 h. For the first additional SMIr batch test set, using procedures previously described, solution was completely removed from each of the six centrifuge tubes and analyzed for NO_3^- -N so as to quantify the amount of NO_3^- removed from solution by SMIr. A 50 mL amount of 1 mole L^{-1} KCl extraction solution was then added to the SMIr remaining in each of the six centrifuge tubes of this first additional test set. The KCl extraction solution and SMIr contained in each centrifuge tube were in turn mixed for 1 h on the laboratory rotator. Next, samples of the KCl extraction

solution were removed from the centrifuge tubes and analyzed for NO_3^- -N so as to determine the amount of NO_3^- adsorbed onto SMIr particle surfaces. With regard to the second additional SMIr batch test set, solution was completely removed from each of the six centrifuge tubes and analyzed for ammonia/ammonium as a means to evaluate whether or not SMIr converts the NO_3^- originally present into ammonia/ammonium. Solution concentrations of ammonia/ammonium ($\text{NH}_3/\text{NH}_4^+$) were analyzed by an outside laboratory (Service Testing and Research Laboratory, Ohio State University, Wooster, Ohio) using micro-Kjeldahl distillation methods (Mulvaney, 1996).

RESULTS AND DISCUSSION

Batch test results are given in tables 3, 4, and 5. Tables 3a and 4a include information on batch test conditions with respect to pH, electrical conductivity (EC), and oxidation/reduction potential (ORP). Most importantly, tables 3a and 4a provide values for percent reduction of nitrate-N (NO_3^- -N), phosphate-P (PO_4^{3-} -P), and atrazine (immunoassay and GC-MS measurements). Again, the pH and ORP values for the filter material batch tests are single replicate measurements, while the pH and ORP quantities for the control batch tests, which include averages and standard deviations (in parentheses), were determined from six replicates. Values in tables 3a and 4a related to EC and percent nutrient/pesticide removal include averages and standard deviations (in parentheses) for sets of six replicate batch tests conducted with each filter material (or no filter

Table 3a. Filter material effectiveness batch test results for three different nutrient/pesticide concentration solutions and 4 h batch test duration. Nutrient/pesticide decrease reported as percent of original amount removed (standard deviations shown in parentheses).

Filter Material	Initial Test Solution Concentration	Final Test Conditions ^[a]			Average % Nutrient/Pesticide Removal			
		pH	EC ^[b] (dS m^{-1})	ORP ^[c] (mV)	NO_3^- -N	PO_4^{3-} -P	Atrazine-1 ^[d]	Atrazine-2 ^[e]
AC	Moderate	8.39	1.88 (0.03)	165	68.5 (0.7)	33.1 (9.3)	100.0 (0.0)	100.0 (0.0)
	High	8.46	2.21 (0.02)	121	65.6 (0.5)	65.2 (3.4)	100.0 (0.0)	100.0 (0.0)
	Extreme	8.52	3.13 (0.03)	125	45.4 (1.1)	88.9 (1.6)	100.0 (0.0)	100.0 (0.0)
FA	Moderate	11.56	9.26 (0.06)	-543	58.5 (1.3)	80.0 (5.0)	100.0 (0.0)	100.0 (0.0)
	High	11.55	10.53 (0.08)	-594	27.2 (0.5)	89.8 (3.3)	99.8 (0.1)	100.0 (0.0)
	Extreme	11.57	9.52 (0.05)	-436	13.8 (0.3)	95.8 (1.3)	100.0 (0.0)	100.0 (0.0)
IS	Moderate	6.49	1.57 (0.03)	-239	90.1 (0.4)	66.3 (4.1)	33.4 (6.0)	43.3 (12.8)
	High	6.29	1.92 (0.03)	-521	89.4 (0.3)	84.0 (0.9)	26.6 (6.2)	11.9 (10.6)
	Extreme	6.32	2.96 (0.07)	-353	22.6 (0.5)	88.1 (0.2)	19.3 (2.7)	6.4 (11.3)
SMIr	Moderate	7.21	2.02 (0.05)	-660	99.0 (0.0)	66.3 (3.8)	25.2 (5.9)	71.3 (6.1)
	High	7.62	2.52 (0.02)	-691	97.5 (0.1)	88.7 (6.1)	35.9 (3.7)	43.3 (3.7)
	Extreme	7.34	3.59 (0.02)	-717	96.6 (0.3)	93.7 (1.4)	40.1 (3.0)	56.9 (5.6)
SMZeo	Moderate	7.23	1.12 (0.03)	96	79.6 (0.5)	87.1 (0.8)	54.2 (5.1)	80.2 (5.8)
	High	7.10	1.71 (0.03)	96	64.5 (0.3)	92.4 (2.7)	48.9 (1.0)	76.7 (5.6)
	Extreme	7.01	10.36 (0.02)	120	41.2 (0.9)	96.5 (0.6)	49.1 (1.3)	79.7 (1.2)
NFM ^[f]	Moderate	8.99 (0.03)	1.10 (0.02)	40.7 (1.5)	-1.1 (0.1)	30.4 (4.8)	-17.2 (7.0)	62.5 (32.0)
	High	8.52 (0.05)	1.59 (0.02)	173.3 (2.2)	-4.1 (0.3)	11.2 (3.6)	13.7 (11.8)	-9.9 (12.9)
	Extreme	8.81 (0.04)	2.62 (0.01)	58.7 (1.5)	-4.2 (0.3)	5.0 (1.9)	17.1 (2.1)	-7.9 (17.8)

^[a] Standard deviations of final test conditions available only for EC, NFM-pH, and NFM-ORP.

^[b] Electrical conductivity (EC) of solution measured in decisiemens per meter (dS m^{-1}).

^[c] Oxidation/reduction potential (ORP) of solution measured in millivolts (mV).

^[d] Atrazine measured with immunoassay methods.

^[e] Atrazine measured with gas chromatograph - mass spectrometer (GC-MS).

^[f] Control batch tests with no filter material present.

Table 3b. Filter material effectiveness batch test results for three different nutrient/pesticide concentration solutions and 4 h batch test duration. Nutrient/pesticide decrease reported as reduction in concentration (nutrient/pesticide concentration remaining shown in parentheses).

Filter Material	Initial Test Solution Concentration	Average Nutrient/Pesticide Concentration Reduction (Average Concentration Remaining) (mg L ⁻¹)			
		NO ₃ ⁻ -N	PO ₄ ³⁻ -P	Atrazine-1 ^[a]	Atrazine-2 ^[b]
AC	Moderate	6.9 (3.1)	0.033 (0.067)	0.100 (0.000)	0.100 (0.000)
	High	32.8 (17.2)	0.163 (0.087)	0.400 (0.000)	0.400 (0.000)
	Extreme	90.8 (109.2)	0.889 (0.111)	0.500 (0.000)	0.500 (0.000)
FA	Moderate	5.9 (4.1)	0.081 (0.019)	0.100 (0.000)	0.100 (0.000)
	High	13.6 (36.4)	0.225 (0.025)	0.399 (0.001)	0.400 (0.000)
	Extreme	27.6 (172.4)	0.958 (0.042)	0.500 (0.000)	0.500 (0.000)
IS	Moderate	9.0 (1.0)	0.066 (0.034)	0.033 (0.067)	0.043 (0.057)
	High	44.7 (5.3)	0.210 (0.040)	0.106 (0.294)	0.048 (0.352)
	Extreme	45.2 (154.8)	0.881 (0.119)	0.097 (0.403)	0.032 (0.468)
SMIr	Moderate	9.9 (0.1)	0.066 (0.034)	0.025 (0.075)	0.071 (0.029)
	High	48.9 (1.1)	0.222 (0.028)	0.144 (0.256)	0.173 (0.227)
	Extreme	193.2 (6.8)	0.937 (0.063)	0.201 (0.299)	0.285 (0.215)
SMZeo	Moderate	8.0 (2.0)	0.087 (0.013)	0.054 (0.046)	0.080 (0.020)
	High	32.3 (17.7)	0.231 (0.019)	0.196 (0.204)	0.307 (0.093)
	Extreme	82.4 (117.6)	0.965 (0.035)	0.246 (0.254)	0.399 (0.101)
NFM ^[c]	Moderate	-0.1 (10.1)	0.030 (0.070)	-0.017 (0.117)	0.063 (0.037)
	High	-2.1 (52.1)	0.028 (0.222)	0.055 (0.345)	-0.040 (0.440)
	Extreme	-8.4 (208.4)	0.050 (0.950)	0.086 (0.414)	-0.040 (0.540)

^[a] Atrazine measured with immunoassay methods.

^[b] Atrazine measured with gas chromatograph - mass spectrometer (GC-MS).

^[c] Control batch tests with no filter material present.

Table 4a. Filter material efficiency batch test results for three different batch test durations with high-concentration solution used in all cases. Nutrient/pesticide decrease reported as percent of original amount removed (standard deviations shown in parentheses).

Filter Material	Batch Test Duration (h)	Final Test Conditions ^[a]			Average % Nutrient/Pesticide Removal			
		pH	EC ^[b] (dS m ⁻¹)	ORP ^[c] (mV)	NO ₃ ⁻ -N	PO ₄ ³⁻ -P	Atrazine-1 ^[d]	Atrazine-2 ^[e]
AC	24	8.34	2.29 (0.01)	143	62.1 (1.1)	70.6 (3.0)	99.7 (0.3)	100.0 (0.0)
	4	8.46	2.21 (0.02)	121	65.6 (0.5)	65.2 (3.4)	100.0 (0.0)	100.0 (0.0)
	1	8.50	2.17 (0.03)	154	63.0 (0.5)	67.6 (11.8)	100.0 (0.0)	100.0 (0.0)
FA	24	11.57	7.83 (0.06)	-298	74.5 (1.6)	94.6 (2.3)	100.0 (0.0)	100.0 (0.0)
	4	11.55	10.53 (0.08)	-594	27.2 (0.5)	89.8 (3.3)	99.8 (0.1)	100.0 (0.0)
	1	11.56	9.12 (0.04)	-581	16.1 (0.5)	96.1 (1.2)	99.1 (1.0)	99.7 (0.6)
IS	24	6.79	1.90 (0.01)	-413	86.3 (0.1)	99.0 (0.6)	25.2 (4.1)	28.0 (6.0)
	4	6.29	1.92 (0.03)	-521	89.4 (0.3)	84.0 (0.9)	26.6 (6.2)	11.9 (10.6)
	1	6.27	1.82 (0.03)	-331	84.3 (0.8)	84.6 (2.2)	24.7 (4.1)	8.5 (7.3)
SMIr	24	7.92	2.19 (0.05)	-733	98.6 (0.3)	94.0 (0.7)	61.8 (5.8)	82.5 (2.1)
	4	7.62	2.52 (0.02)	-691	97.5 (0.1)	88.7 (6.1)	35.9 (3.7)	43.3 (3.7)
	1	7.39	2.51 (0.04)	-652	96.0 (0.1)	69.2 (27.5)	17.2 (3.7)	23.0 (16.0)
SMZeo	24	6.98	1.56 (0.04)	113	66.0 (0.4)	92.3 (1.4)	59.9 (2.6)	82.8 (1.2)
	4	7.10	1.71 (0.03)	96	64.5 (0.3)	92.4 (2.7)	48.9 (1.0)	76.7 (5.6)
	1	7.19	1.60 (0.03)	111	62.7 (0.2)	88.0 (0.3)	43.8 (3.3)	71.5 (2.8)
NFM ^[f]	24	7.38 (1.43)	1.53 (0.07)	166.6 (8.8)	-0.3 (1.2)	8.3 (9.3)	11.1 (12.7)	-10.6 (10.3)
	4	8.52 (0.05)	1.59 (0.02)	173.3 (2.2)	-4.1 (0.3)	11.2 (3.6)	13.7 (11.8)	-9.9 (12.9)

^[a] Standard deviations of final test conditions available only for EC, NFM-pH, and NFM-ORP.

^[b] Electrical conductivity of solution.

^[c] Oxidation/reduction potential of solution.

^[d] Atrazine measured with immunoassay methods.

^[e] Atrazine measured with gas chromatograph - mass spectrometer (GC-MS).

^[f] Control batch tests with no filter material present.

material), test solution, and test duration combination. With very few exceptions, the standard deviation values shown in tables 3a and 4a are relatively small, indicating that the results within any particular batch test set tend to be very consistent. Tables 3b and 4b list the NO₃⁻-N, PO₄³⁻-P, and atrazine (immunoassay and GC-MS) results as average concentration reduction values and average concentration

remaining values (in parentheses). Each average value in tables 3b and 4b was calculated from measurements obtained from six batch test replicates.

Tables 3a and 3b provide information on filter material contaminant removal effectiveness, based on testing the five filter materials against moderate, high, and extreme initial nutrient/pesticide levels that varied, respectively, from 10 to

Table 4b. Filter material efficiency batch test results for three different batch test durations, with high-concentration solution used in all cases. Nutrient/pesticide decrease reported as reduction in concentration (nutrient/pesticide concentration remaining shown in parentheses).

Filter Material	Batch Test Duration (h)	Average Nutrient/Pesticide Concentration Reduction (Average Concentration Remaining) (mg L ⁻¹)			
		NO ₃ ⁻ -N	PO ₄ ³⁻ -P	Atrazine-1 ^[a]	Atrazine-2 ^[b]
AC	24	31.1 (18.9)	0.177 (0.073)	0.399 (0.001)	0.400 (0.000)
	4	32.8 (17.2)	0.163 (0.087)	0.400 (0.000)	0.400 (0.000)
	1	31.5 (18.5)	0.169 (0.081)	0.400 (0.000)	0.400 (0.000)
FA	24	37.3 (12.7)	0.237 (0.013)	0.400 (0.000)	0.400 (0.000)
	4	13.6 (36.4)	0.225 (0.025)	0.399 (0.001)	0.400 (0.000)
	1	8.1 (41.9)	0.240 (0.010)	0.396 (0.004)	0.399 (0.001)
IS	24	43.2 (6.8)	0.248 (0.002)	0.101 (0.299)	0.112 (0.288)
	4	44.7 (5.3)	0.210 (0.040)	0.106 (0.294)	0.048 (0.352)
	1	42.2 (7.8)	0.212 (0.038)	0.099 (0.301)	0.034 (0.366)
SMIr	24	49.3 (0.7)	0.235 (0.015)	0.247 (0.153)	0.330 (0.070)
	4	48.9 (1.1)	0.222 (0.028)	0.144 (0.256)	0.173 (0.227)
	1	48.0 (2.0)	0.173 (0.077)	0.069 (0.331)	0.092 (0.308)
SMZeo	24	33.0 (17.0)	0.231 (0.019)	0.240 (0.160)	0.331 (0.069)
	4	32.3 (17.7)	0.231 (0.019)	0.196 (0.204)	0.307 (0.093)
	1	31.4 (18.6)	0.220 (0.030)	0.175 (0.225)	0.286 (0.114)
NFM ^[c]	24	-0.2 (50.2)	0.021 (0.229)	0.044 (0.356)	-0.042 (0.442)
	4	-2.1 (52.1)	0.028 (0.222)	0.055 (0.345)	-0.040 (0.440)

[a] Atrazine measured with immunoassay methods.

[b] Atrazine measured with gas chromatograph - mass spectrometer (GC-MS).

[c] Control batch tests with no filter material present.

Table 5. Results from batch tests conducted to determine the SMIr process for nitrate removal (all values in mg L⁻¹).

	NO ₃ ⁻ -N (Batch Test Solution)	NO ₃ ⁻ -N (KCl Extraction Solution)	NH ₃ -N or NH ₄ ⁺ -N (Batch Test Solution)
Average	7.8	0.0	156.9
SD	2.6	0.0	2.9

50 to 200 mg L⁻¹ for NO₃⁻-N, from 0.1 to 0.25 to 1.0 mg L⁻¹ for PO₄³⁻-P, and from 0.1 to 0.4 to 0.5 mg L⁻¹ for atrazine. As previously mentioned, all batch tests that focused on evaluating filter material effectiveness had 4 h durations. Tables 4a and 4b present information on filter material contaminant removal efficiency, which was assessed by testing the five filter materials against the high-concentration nutrient/pesticide solution for three different exposure times (batch test durations) of 24, 4, and 1 h. It is important to note that the high-concentration solution, 4 h batch tests were used for investigating both the effectiveness and the efficiency of the filter materials. Therefore, the data from these tests are included in tables 3a and 3b and in tables 4a and 4b.

Table 5 provides the results of two additional batch test sets that were conducted to gain insight on the nitrate removal mechanism for sulfur-modified iron (SMIr). Tabulated data are included on the amount of NO₃⁻-N remaining in solution after exposure to SMIr, the amount of extracted NO₃⁻-N that remained adsorbed onto SMIr particle surfaces, and the amount of NO₃⁻-N that was converted by SMIr to ammonia/ammonium-nitrogen (NH₃/NH₄⁺-N). The average and standard deviation of the measured NO₃⁻-N and NH₃/NH₄⁺-N amounts are given in table 5 as solution concentration values (mg L⁻¹).

CONTROL (NFM) BATCH TESTS

Results for the control batch test sets (six replicates) conducted without filter material are provided in tables 3a,

3b, 4a, and 4b, and the general notation used in these tables to designate the control tests is NFM. Tables 3a and 4a show that the final pH, electrical conductivity (EC), and oxidation/reduction potential (ORP) test condition averages for the control batch test sets had a pH range from 7.38 to 8.99, an EC range from 1.10 to 2.62 dS m⁻¹, and an ORP range from 40.7 to 173.3 mV. As might be expected, NO₃⁻-N concentrations remained near initial levels for all the control batch tests. The largest nitrate (NO₃⁻) deviation was found for the extreme-concentration solution, 4 h control batch test set, which had an average measured concentration of 208.4 mg L⁻¹ NO₃⁻-N compared to the initial solution concentration of 200 mg L⁻¹ NO₃⁻-N (a -4.2% difference).

A generally small average phosphate (PO₄³⁻) loss, uniformly between 0.021 to 0.050 mg L⁻¹ PO₄³⁻-P, was observed for all control batch test sets (tables 3b and 4b). With respect to percent removal (tables 3a and 4a), this control batch test PO₄³⁻ loss was 12% or less, with one exception, and that exception was the moderate concentration, 4 h control batch test set, which exhibited an average PO₄³⁻ loss of 30.4% (equal to a concentration reduction of 0.030 mg L⁻¹ PO₄³⁻-P; table 3b). Interpreting the moderate concentration, 4 h control batch test PO₄³⁻-P results for the five filter materials, especially in terms of percent removal, will therefore require taking into account the experimental method PO₄³⁻-P losses revealed by the control batch tests.

The average percent atrazine reduction for the control batch test sets, determined via immunoassay or GC-MS methods, ranged in value from -17.2% to 17.1% for all but one case (tables 3a and 4a). The exception, with regard to atrazine, was the moderate concentration, 4 h control batch test set measured with GC-MS methods, which exhibited an average atrazine reduction of 62.5%. Consequently, the validity of the GC-MS atrazine results, for all moderate concentration, 4 h batch test sets, with or without filter

material, needs to be carefully considered, and probably should not be given nearly as much importance as the corresponding immunoassay atrazine results. Actual deviations of the control batch test set atrazine averages (immunoassay and GC-MS) compared to initial solution concentrations ranged from -0.042 to 0.086 mg L^{-1} (tables 3b and 4b). Negative average values of percent nutrient/pesticide removal or concentration reduction, found only with the control batch test sets, simply indicate that for a particular batch test set, the measured nutrient/pesticide concentrations at test completion were higher than the initial solution nutrient/pesticide concentration. Overall, with the two exceptions already noted, the control batch tests indicate that the nutrient/pesticide measurement errors and/or the nutrient/pesticide losses due to experimental methods are within acceptable limits and will not prevent the basic evaluation of filter material effectiveness and efficiency for removing agricultural contaminants from water.

ACTIVATED CARBON (AC) BATCH TESTS

The steam activated carbon (AC) batch test sets had final pH/EC/ORP test conditions ranging from 8.34 to 8.52 for pH, from 1.88 to 3.13 dS m^{-1} for EC, and from 121 to 165 mV for ORP (tables 3a and 4a). The EC values for the AC tests were slightly higher than the corresponding EC values for the control batch tests, which indicates that AC released small amounts of dissolved cations and anions into the original nutrient/pesticide solutions. The AC filter material proved capable of removing significant amounts of NO_3^- . With respect to the effectiveness of AC nitrate removal, tested against the moderate, high, and extreme concentration solutions and a 4 h exposure time, the NO_3^- -N reductions were, respectively, 68.5%, 65.6%, and 45.4%, or 6.9, 32.8, and 90.8 mg L^{-1} (tables 3a and 3b). The AC filter material could therefore be considered moderately effective in removing NO_3^- , and the total amount of NO_3^- removed increased as the initial NO_3^- concentration increased. Nitrate treatment by AC is fairly efficient in regard to quick removal, as indicated by the average 63.0% NO_3^- -N decrease measured for the 1 h tests with the high-concentration solution. The average NO_3^- -N reductions for the high-concentration solution varied only from 62.1% to 65.6% (31.1 to 32.8 mg L^{-1} concentration decrease) for batch test durations of 24, 4, and 1 h, which showed again, from an efficiency perspective, that reactions between AC and NO_3^- were not time dependent, at least over the exposure times tested (tables 4a and 4b). Thought of in a somewhat different manner, the stable NO_3^- -N removal values indicate that chemical equilibrium conditions were achieved for interactions between AC and NO_3^- within 1 h of exposure time between AC and NO_3^- .

Electrolyte compounds containing NO_3^- tend to be extremely soluble, so chemical precipitates that incorporate NO_3^- are unlikely to form (McBride, 1994). The AC results for NO_3^- are therefore best explained by a non-specific adsorption process in which nitrate anions are electrostatically attracted to positively charged oxygen functional group sites that are present on AC particle surfaces (Marsh and Rodriguez-Reinoso, 2006; Tsang et al., 2007). Ion exchange reactions, such as NO_3^- electrostatic adsorption at positively charged particle surface sites, tend to be extremely fast (McBride, 1994). Even though AC batch test

pH values were somewhat high (8.34 to 8.52), positive charge would develop at functional group surface sites if the point of zero charge (PZC) for AC was above 8.52, which is certainly possible (Rivera-Utrilla and Sanchez-Polo, 2002; Giraldo and Moreno-Pirajan, 2007; Srivastava et al., 2008).

The AC removal effectiveness for PO_4^{3-} -P increased with increasing initial concentration of PO_4^{3-} -P (tables 3a and 3b). (However, it is in fact possible that AC removed very little PO_4^{3-} -P from the moderate-concentration solution, since the amount of PO_4^{3-} -P removed during the moderate-concentration solution control batch tests was on average similar to the amount of PO_4^{3-} -P removed during the moderate-concentration solution AC batch tests.) The AC filter material can be very efficient in removing PO_4^{3-} -P, based on an average PO_4^{3-} -P reduction of 67.6% exhibited by the 1 h batch tests with the high-concentration solution. Also from an efficiency standpoint, as shown in tables 4a and 4b, the AC-affected PO_4^{3-} -P reduction for the high-concentration solution was not time dependent (at least for the range of exposure times tested) because PO_4^{3-} -P reductions varied only from 65.2% to 70.6% (0.163 to 0.177 mg L^{-1} concentration decrease) over the three test durations of 24, 4, and 1 h. Essentially, chemical equilibrium conditions existed for AC and PO_4^{3-} interactions within a 1 h exposure time.

Assuming that significant amounts of mobile calcium, iron, or aluminum cations are available, a possible mechanism that accounts for AC removal of PO_4^{3-} from solution is the formation of calcium/iron/aluminum-phosphate chemical precipitates (Bohn et al., 1985). The more probable removal mechanism is ligand exchange of PO_4^{3-} at oxygen functional groups that are present on AC particle surfaces (Bohn et al., 1985). The PO_4^{3-} -P results for the moderate-concentration, 4 h AC batch tests (which were similar to those of the moderate-concentration, 4 h control batch tests) indicate that an initial PO_4^{3-} -P level of 0.1 mg L^{-1} is not sufficient to produce substantial amounts of AC-affected phosphate precipitates or cause PO_4^{3-} loss due to ligand exchange on AC particle surfaces. Either the equilibrium PO_4^{3-} -P concentration for a solution in contact with the phosphate precipitates was around 0.1 mg L^{-1} or greater (and consequently no precipitate was formed with the moderate-concentration solution because its initial PO_4^{3-} -P level of 0.1 mg L^{-1} was too low), or alternatively, there were just not enough phosphate ions present with the moderate-concentration solution to effectively compete for the AC oxygen functional group sites.

Perhaps most importantly, AC was one of the two filter materials (the other was the fly ash) that were most effective and efficient in removing the pesticide, atrazine, from solution. Regardless of the initial concentration level and test duration exposure time, AC essentially removed 100% of the atrazine originally present in solution, showing that AC has the potential to quickly and completely remove pesticides from drainage waters (tables 3a, 3b, 4a, and 4b). It is possible that 100% atrazine removal could have been achieved with batch tests using much less than 5 g of AC. Due to the fast reaction time indicated by the results (tables 4a and 4b), the most probable the mechanism for atrazine reduction was adsorbance of atrazine molecules onto nonpolar AC surfaces via London and van der Waals dispersion forces and hydrophobic interactions (Rosen, 1989; McBride, 1994).

FLY ASH (FA) BATCH TESTS

The high calcium oxide-high carbon fly ash (FA) had final batch test pH/EC/ORP conditions ranging from 11.55 to 11.57 for pH, from 7.83 to 10.53 dS m⁻¹ for EC, and from -594 to -298 mV for ORP. The EC values for the FA tests were substantially higher than the corresponding EC values for the control batch tests, which indicates that soluble components of FA released large amounts of dissolved cations and anions into the original nutrient/pesticide solutions. Table 3a shows that the effectiveness of FA for nitrate removal, at least with respect to percent NO₃⁻-N decrease, was greatest for the moderate-concentration solution (58.5% NO₃⁻-N decrease) and was least effective with the extreme-concentration solution (13.8% NO₃⁻-N decrease). However, when evaluated on the basis of nitrate concentration reduction, the 5.9 mg L⁻¹ NO₃⁻-N decrease for the moderate-concentration solution was lowest and the 27.6 mg L⁻¹ NO₃⁻-N decrease for the extreme-concentration solution was the highest (table 3b). The NO₃⁻-N average percent removal decreased from 74.6% to 27.2% to 16.1% as the batch test exposure time between FA and the high-concentration solution decreased from 24 to 4 to 1 h (table 4a). The NO₃⁻-N concentration reduction decreased from 37.3 to 13.6 to 8.1 mg L⁻¹ as the batch test exposure time between FA and the high-concentration solution decreased from 24 to 4 to 1 h (table 4b). Hence, with respect to efficiency, NO₃⁻ removal by FA is very much time dependent (chemical non-equilibrium) and only a small fraction of the NO₃⁻ originally present can be removed by FA during a short 1 h time period. These findings indicate that FA is not a particularly efficient filter material for NO₃⁻ water treatment.

Fly ash materials typically contain significant amounts of calcium/iron/aluminum oxides (Hausmann, 1990). The calcium/iron/aluminum oxides originally present within FA and/or the calcium/iron/aluminum oxides/hydroxides formed by FA exposure to the nutrient/pesticide solutions could provide functional group sites for electrostatic NO₃⁻ adsorption. However, since these minerals have PZC values generally well below the pH values (11.55 to 11.57) of the FA batch tests (Stumm and Morgan, 1981; Sparks, 2003), positive charge would not likely develop at most of these functional group sites, in turn preventing substantial electrostatic adsorption of NO₃⁻. Therefore, non-specific electrostatic adsorption of nitrate anions at positively charged functional group sites on FA particle surfaces is probably not the mechanism by which NO₃⁻ is removed by FA. Alternatively, the FA batch test ORP values were low (-594 to -298 mV), so redox conditions could have been conducive for nitrate removal via electrochemical reduction of NO₃⁻ to ammonium (NH₄⁺) or nitrogen gas (N₂) (Drever, 1982; McBride, 1994).

The FA filter material was one of two (surfactant-modified zeolite was the other) that were the most effective and efficient in removing PO₄³⁻ from solution. The average percent PO₄³⁻-P reduction was 80.0% or greater for all batch test sets conducted with FA. (Note: Taking into account the results of the moderate-concentration, 4 h control batch tests, the percent PO₄³⁻-P reduction for the moderate-concentration, 4 h FA batch test may actually have been closer to 50%.) Consequently, FA proved not only to be effective for removing at least half of the PO₄³⁻ present, regardless of the initial PO₄³⁻-P solution concentration (tables 3a and 3b), but it also exhibited efficiency for rapid

PO₄³⁻ removal, as shown by the 96.1% PO₄³⁻-P decrease (0.240 mg L⁻¹ PO₄³⁻-P concentration decrease) during the 1 h batch tests with the high-concentration solution (tables 4a and 4b). In addition, the relatively stable PO₄³⁻-P removal values for FA shown in tables 4a and 4b indicate that chemical equilibrium conditions were achieved for interactions between FA and PO₄³⁻ within a 1 h exposure time between FA and PO₄³⁻.

Even with the low redox conditions present during the FA batch tests, given that there is probably a sufficient amount of dissolved aluminum present, PO₄³⁻ removal by FA could plausibly be due to the formation calcium/iron/aluminum-phosphate chemical precipitates or ligand exchange of PO₄³⁻ at functional group sites on calcium/iron/aluminum oxide/hydroxide surfaces (Murray and Hesterberg, 2006). Although low redox conditions were present in the FA tests, electrochemical reduction of PO₄³⁻ (with phosphorus as the electron acceptor) is unlikely to occur (Bohn et al., 1985). The ligand exchange and/or precipitation mechanisms that best explain FA removal of PO₄³⁻ exhibit increased intensity with respect to percent PO₄³⁻-P removal as the initial PO₄³⁻-P concentration increases, as was also the case to a greater or lesser extent for the AC, iron sulfide (IS), and sulfur-modified iron (SMIr) filter materials.

In addition, FA was one of the two most effective and efficient filter materials for removing atrazine (the other was AC). The average percent atrazine reduction was greater than 99% for all FA batch test sets. (It is possible that close to 100% atrazine removal could have been achieved with batch tests using much less than 5 g of FA.) The atrazine results presented for FA in tables 3a, 3b, 4a, and 4b clearly indicate that this filter material has the potential to quickly and completely remove pesticides from drainage waters.

Two different processes can account for atrazine removal by FA. First, the FA material is a high carbon fly ash, and the nonpolar carbon surfaces present could provide sites for atrazine adsorption via London and van der Waals dispersion forces and hydrophobic interactions (Rosen, 1989; McBride, 1994). Second, based on the low FA batch test ORP values measured, redox conditions may have been suitable for atrazine degradation by reductive dechlorination (Shimomura and Sanford, 2005).

The high calcium oxide-high carbon fly ash tested appears to be a promising filter medium in regard to PO₄³⁻ and atrazine removal. However, many fly ash materials tend to form a cemented mass when hydrated (Hausmann, 1990), which can reduce flow capacity for transmitting contaminated water and therefore limit use of these fly ash materials in filter treatment systems. Consequently, to ensure that FA water flow capacity is sufficient, hydraulic conductivity tests need to be conducted with FA alone and/or FA combined with a permeable bulking agent such as clean sand, or even spent foundry sand.

IRON SULFIDE (IS) BATCH TESTS

The iron sulfide filter material (IS), with a chemical formula of FeS, had final pH/EC/ORP test conditions ranging from 6.27 to 6.79 for pH, from 1.57 to 2.96 dS m⁻¹ for EC, and from -521 to -239 mV for ORP. The IS removal effectiveness for NO₃⁻-N (tables 3a and 3b) was very good with respect to the moderate-concentration solution (90.1% decrease, 9.0 mg L⁻¹ concentration reduction) and the high-concentration solution (89.4% decrease, 44.7 mg L⁻¹

concentration reduction), but not nearly as impressive for the extreme-concentration solution (only a 22.6% decrease, 45.2 mg L⁻¹ concentration reduction). Based on similar IS-affected NO₃⁻-N concentration reductions for the high-concentration, 4 h tests and the extreme-concentration, 4 h tests (average decreases of 44.7 and 45.2 mg L⁻¹, respectively), there seems to be a limit to the amount on NO₃⁻ removed by IS once the initial NO₃⁻ concentration gets above a certain level. Nitrate treatment by IS was shown to be extremely efficient in regard to quick removal, as indicated by the average 84.3% NO₃⁻-N decrease measured for the 1 h tests with the high-concentration solution. The average NO₃⁻-N reductions for the high-concentration solution varied only between 84.3% to 89.4% (42.2 to 44.7 mg L⁻¹ concentration decrease) for batch test durations of 24, 4, and 1 h, which showed, also from the standpoint of efficiency, that reactions between IS and NO₃⁻ were not time dependent (chemical equilibrium conditions existed for IS and NO₃⁻ interactions) over the range of exposure times tested (tables 4a and 4b).

The process by which IS removes NO₃⁻ from solution is not entirely clear, but there are a couple of possibilities. Even under low redox conditions, if a sufficient amount of dissolved iron is released into the solution by IS, then iron oxide/hydroxide minerals could form that have functional groups sites where NO₃⁻ could be electrostatically adsorbed (Stumm and Morgan, 1981; Bohn et al., 1985; Drever, 1982). The low ORP values measured for the IS batch tests might also potentially be a factor with respect to IS removal of NO₃⁻ because low ORP values may indicate that redox conditions are conducive for nitrate removal via electrochemical reduction of NO₃⁻ to NH₄⁺ or N₂ (Drever, 1982).

The IS filter material appears to be reasonably effective for removing PO₄³⁻. The average PO₄³⁻-P removal was 66.3% (0.066 mg L⁻¹ concentration reduction) for the moderate-concentration, 4 h batch tests; 84.0% (0.210 mg L⁻¹ concentration reduction) for the high-concentration, 4 h batch tests; and 88.1% (0.881 mg L⁻¹ concentration reduction) for the extreme-concentration, 4 h batch tests (tables 3a and 3b). (Note: Taking into account the PO₄³⁻-P loss of 0.030 mg L⁻¹ due to experimental methods determined for the moderate-concentration, 4 h control batch tests, the actual average PO₄³⁻-P removal for the moderate-concentration, 4 h batch test set with IS may be closer to 36%, or 0.036 mg L⁻¹.) Efficiency for rapid PO₄³⁻ removal by IS was shown by the 84.6% PO₄³⁻-P decrease (0.212 mg L⁻¹ PO₄³⁻-P concentration decrease) during the 1 h duration batch tests with the high-concentration solution (tables 4a and 4b). Additionally, from an efficiency perspective, there may have been some moderate time dependence regarding IS removal of PO₄³⁻, as demonstrated by an average PO₄³⁻-P percent reduction change from 99.0% to 84.0% to 84.6%, respectively, for the 24, 4, and 1 h batch tests with the high-concentration solution.

With respect to the mechanism for PO₄³⁻ removal by IS, even under low redox conditions, if a sufficient amount of dissolved iron is released into the solution by IS, then iron oxide/hydroxide minerals could form that have functional groups sites where PO₄³⁻ could become attached via ligand exchange (Stumm and Morgan, 1981; Bohn et al., 1985; Drever, 1982). The formation of iron-phosphate precipitates might be another possibility that accounts for PO₄³⁻ removal by IS (Bohn et al., 1985). Although low redox conditions

were present in the IS tests, electrochemical reduction of PO₄³⁻ (with phosphorus as the electron acceptor) is unlikely to occur (Bohn et al., 1985). The ligand exchange and/or precipitation mechanisms that best explain IS removal of PO₄³⁻ exhibit increased intensity with respect to percent PO₄³⁻-P removal as the initial PO₄³⁻-P concentration increases, as was also the case to a greater or lesser extent for the AC, FA, and SMIr filter materials.

The IS filter material was not especially effective or efficient in removing atrazine. Excluding the unreliable average percent atrazine removal value obtained by GC-MS measurements for the moderate-concentration, 4 h batch test set, the greatest average percent atrazine removal for any of the other batch test sets, from either immunoassay or GC-MS measurements, was only 33.4%. Because low redox conditions were present during the IS batch tests, the limited amount of atrazine removal by IS may be accounted for by the process of reductive dechlorination (Shimomura and Sanford, 2005).

SULFUR-MODIFIED IRON (SMIr) BATCH TESTS

The final pH/EC/ORP test condition ranges for the sulfur-modified iron (SMIr) batch test sets were 7.21 to 7.92 for pH, 2.02 to 3.59 dS m⁻¹ for EC, and -733 to -652 mV for ORP. The range of ORP values measured for SMIr were the lowest for any of the filter materials evaluated in this study. Most importantly, SMIr proved to be the most effective and efficient filter material for removing NO₃⁻. Regardless of the initial NO₃⁻-N concentration and batch test duration time, SMIr removed greater than 95% of the NO₃⁻-N present in solution (tables 3a, 3b, 4a, and 4b). Chemical equilibrium conditions were obviously reached quite rapidly for interactions involving SMIr and NO₃⁻. Consequently, SMIr appears to be capable of quick and almost complete removal of NO₃⁻ from subsurface drainage waters.

Two additional sets of batch tests were carried out with SMIr to provide insight on the processes by which SMIr removes NO₃⁻ from water. Both of these additional SMIr batch test sets (each with six replicates) were conducted with the extreme-concentration solution (containing 200 mg L⁻¹ NO₃⁻-N) and a 24 h test duration time. For the first additional SMIr batch test set, solution separated from the SMIr after test completion was analyzed to determine the amount of NO₃⁻-N remaining in solution that had not been removed by SMIr. A 50 mL quantity of 1 mole L⁻¹ KCl extraction solution was then mixed with the 5 g of SMIr used for each replicate of this first additional SMIr batch test set. After mixing, the KCl extraction solution was separated from the SMIr and analyzed for NO₃⁻-N to determine the amount of NO₃⁻ adsorbed onto SMIr particle surfaces. With regard to the second additional SMIr batch test set, solution was completely removed from each of the six centrifuge tubes and analyzed for ammonia/ammonium (NH₃/NH₄⁺) as a means to evaluate whether or not SMIr converts the NO₃⁻ originally present into NH₃/NH₄⁺. The results for the two additional SMIr batch test sets are presented in table 5. On average, 96.1% of the NO₃⁻ initially present in the solution was removed; however, none (0.0%) of the NO₃⁻ that was removed remained adsorbed onto SMIr particle surfaces. Furthermore, table 5 indicates that 81.6% of the NO₃⁻ removed was electrochemically reduced to either NH₃ or NH₄⁺, with NH₄⁺ probably being the more likely end product based on zero-valent iron research (Westerhoff and James,

2003; Chen et al., 2005; Lee et al., 2007). The remaining 18.4% NO_3^- removed could be accounted for by electrochemical reduction of NO_3^- to N_2 , again based on zero-valent iron research (Yang and Lee, 2005; Choe et al., 2000). Low-cost, abundant, natural zeolite has been proven very effective/efficient for removing NH_4^+ from water via cation exchange processes (Booker et al., 1996; Demir et al., 2002; Sepaskhah and Yousefi, 2007). Therefore, a two-stage filter treatment system in which drainage water first flows through sulfur-modified iron (to convert NO_3^- to NH_4^+) and then flows through zeolite (to remove the remaining NH_4^+) could be a feasible way for removing inorganic nitrogen originally present in subsurface drainage waters.

Various factors and processes impacting the ability of zero-valent iron to remove NO_3^- may also have a similar impact on sulfur-modified iron removal of NO_3^- . Because iron oxides/hydroxides and green rusts precipitate on zero-valent iron particle surfaces exposed to ground waters (Roh et al., 2000; Phillips et al., 2003; Huang et al., 2003; Haung and Zhang, 2005), it also may be possible for various iron oxides/hydroxides and green rusts to form on sulfur-modified iron exposed to drainage waters. These iron oxides/hydroxides and green rusts have been shown to directly influence the rate and extent that zero-valent iron transforms NO_3^- to NH_4^+ (Huang et al., 2003; Choe et al., 2004). Furthermore, based on results from a laboratory investigation, Yang and Lee (2005) and Rodriguez-Maroto et al. (2009) concluded that zero-valent iron-affected NO_3^- removal is a two-step process in which NO_3^- is first adsorbed on zero-valent iron particle surfaces, followed by transformation of NO_3^- to NH_4^+ . This two-step NO_3^- removal process might also be valid for sulfur-modified iron. Differences exist between zero-valent iron and sulfur-modified iron with respect to NO_3^- removal, and results from this investigation indicate that there may be some very important advantages to using sulfur-modified iron instead of zero-valent iron for NO_3^- water treatment. First, zero-valent iron-assisted electrochemical reduction of NO_3^- to NH_4^+ can be greatly enhanced by providing a low pH environment ($\text{pH} \leq 4$) (Huang et al., 1998; Chen et al., 2005); however, tables 3a and 4a combined with table 5 show that a low pH environment is not needed for SMIr to effectively and efficiently transform NO_3^- to NH_4^+ . Second, zero-valent iron-assisted electrochemical reduction of NO_3^- to NH_4^+ can also be substantially enhanced by adding soluble ferrous iron (Fe^{2+}) to the filter treatment environment (Huang et al., 2003; Haung and Zhang, 2005); again however, tables 3a and 4a combined with table 5 clearly indicate that SMIr effectively and efficiently removes NO_3^- by itself, without the addition of soluble Fe^{2+} .

The effectiveness and efficiency trends for PO_4^{3-} removal that were found for SMIr were similar to the trends observed for IS. Much the same as IS, the SMIr filter material was reasonably effective for removing PO_4^{3-} . The average PO_4^{3-} -P removal was 66.3% (0.066 mg L^{-1} concentration reduction) for the moderate-concentration, 4 h batch tests; 88.7% (0.222 mg L^{-1} concentration reduction) for the high-concentration, 4 h batch tests; and 93.7% (0.937 mg L^{-1} concentration reduction) for the extreme-concentration, 4 h batch tests (tables 3a and 3b). (Note: Taking into account the PO_4^{3-} -P loss of 0.030 mg L^{-1} due to experimental methods determined for the moderate-concentration, 4 h control batch tests, the actual average PO_4^{3-} -P removal for the moderate-

concentration, 4 h batch test set with SMIr may be closer to 36%, or 0.036 mg L^{-1} .) Efficiency for rapid PO_4^{3-} removal by SMIr was shown by the 69.2% PO_4^{3-} -P decrease (0.173 mg L^{-1} PO_4^{3-} -P concentration decrease) during the 1 h duration batch tests with the high-concentration solution (tables 4a and 4b). Additionally, from an efficiency perspective, there was substantial time dependence (chemical non-equilibrium) exhibited for SMIr removal of PO_4^{3-} , as demonstrated by an average percent PO_4^{3-} -P decrease of 94.0%, 88.7%, and 69.2%, respectively, for the 24, 4, and 1 h batch tests with the high-concentration solution.

The same PO_4^{3-} removal mechanisms proposed for IS are likely to also apply for SMIr. Even given the low redox conditions observed for the SMIr batch tests, but assuming that a sufficient amount of dissolved iron is released into the solution by SMIr, iron oxide/hydroxide minerals could form that have functional groups sites where PO_4^{3-} could become attached via ligand exchange (Stumm and Morgan, 1981; Bohn et al., 1985; Drever, 1982). The formation of iron-phosphate precipitates might be another possibility that accounts for PO_4^{3-} removal by SMIr (Bohn et al., 1985). Although low redox conditions were present in the SMIr tests, electrochemical reduction of PO_4^{3-} (with phosphorus as the electron acceptor) is unlikely to occur (Bohn et al., 1985). The ligand exchange and/or precipitation mechanisms that best explain SMIr removal of PO_4^{3-} exhibit increased intensity with respect to percent PO_4^{3-} -P removal as the initial PO_4^{3-} -P concentration increases, as was also the case to a greater or lesser extent for the AC, FA, and IS filter materials.

As with IS, the SMIr filter material does not seem to be overly effective or efficient for removing atrazine. Excluding the unreliable average percent atrazine removal value obtained by GC-MS measurements for the moderate-concentration, 4 h batch test set, the greatest average percent atrazine removal for any of the other batch test sets, from either immunoassay or GC-MS measurements, was only 61.8%. Because low redox conditions were present during the SMIr batch tests, the limited amount of atrazine removal by SMIr may be accounted for by the process of reductive dechlorination (Shimomura and Sanford, 2005).

SURFACTANT-MODIFIED ZEOLITE (SMZeo) BATCH TESTS

The surfactant-modified zeolite (SMZeo) batch test sets had final pH/EC/ORP test conditions ranging from 6.89 to 7.23 for pH, from 1.12 to 10.36 dS m^{-1} for EC, and from 96 to 120 mV for ORP (tables 3a and 4a). The average EC for the extreme-concentration, 4 h batch test set with SMZeo was the second highest found during this study, and much higher than the average EC values for the other SMZeo batch test sets. The effectiveness of SMZeo for nitrate removal, at least with respect to the percent NO_3^- -N decrease shown in table 3a, was greatest for the moderate-concentration solution (79.6% NO_3^- -N decrease) and was least effective with the extreme-concentration solution (41.2% NO_3^- -N decrease). However, when evaluated on the basis of nitrate concentration reduction, the 8.0 mg L^{-1} NO_3^- -N decrease for the moderate-concentration solution was lowest and the 82.4 mg L^{-1} NO_3^- -N decrease for the extreme-concentration solution was the highest (table 3b). Nitrate treatment by SMZeo was particularly efficient in regard to quick removal, as indicated by the average 62.7% NO_3^- -N decrease

measured for the 1 h tests with the high-concentration solution. Also from an efficiency standpoint, the average NO_3^- -N reductions for the high-concentration solution varied only between 62.7% to 66.0% (31.4 to 33.0 mg L^{-1} concentration decrease) for batch test durations of 24, 4, and 1 h, which implies that reactions between SMZeo and NO_3^- were not time dependent over the exposure times tested (tables 4a and 4b). Consequently, chemical equilibrium conditions existed for SMZeo and NO_3^- interactions within a 1 h exposure time.

The most likely process accounting for the rapid removal of NO_3^- by SMZeo is electrostatic adsorption of nitrate anions at positively charged sites on particle surfaces. Treating zeolite materials with a large amount of cationic surfactant results in the formation of surfactant bilayers on zeolite surfaces (Sullivan et al., 1997; Bowman, 2003). Surface charge reversals, from negative to positive, occur where these surfactant bilayers form (fig. 1). In places on zeolite surfaces where surfactant bilayers have formed, the surfactant/water interface becomes a potential site for electrostatic adsorption of anions, such as NO_3^- (Li and Bowman, 2001; Bowman, 2003; Bansiwali et al., 2006).

The SMZeo filter material was one of two materials (FA was the other) that were the most effective and efficient in removing PO_4^{3-} from solution. The average percent PO_4^{3-} -P reduction was greater than 87% for all batch test sets conducted with SMZeo. (Note: Taking into account the results of the moderate-concentration, 4 h control batch tests, the percent PO_4^{3-} -P reduction for the moderate-concentration, 4 h SMZeo batch test may actually have been closer to 57%.) Consequently, SMZeo proved not only to be effective for removing more than half of the PO_4^{3-} present, regardless of the initial PO_4^{3-} -P solution concentration (tables 3a and 3b), but it also exhibited efficiency for rapid PO_4^{3-} removal, as shown by the 88.0% PO_4^{3-} -P decrease (0.220 mg L^{-1} PO_4^{3-} -P concentration decrease) during the 1 h duration batch tests with the high-concentration solution (tables 4a and 4b). Also from an efficiency standpoint, as shown in tables 4a and 4b, the SMZeo-affected PO_4^{3-} -P reduction for the high-concentration solution was not time dependent (at least for the range of exposure times tested) because PO_4^{3-} -P reductions varied only between 88.0% to 92.4% (0.220 to 0.231 mg L^{-1} concentration decrease) for batch test durations of 24, 4, and 1 h. (Chemical equilibrium conditions therefore existed for SMZeo and PO_4^{3-} interactions within a 1 h exposure time.) As was previously discussed with regard to NO_3^- removal by SMZeo, the process by which PO_4^{3-} is removed from solution is probably due to surface charge reversal from negative to positive due to surfactant bilayer coating of the zeolite, which in turn promotes electrostatic adsorption of negatively charged anions, such as PO_4^{3-} (Li and Bowman, 2001; Bowman, 2003; Bansiwali et al., 2006).

The surfactant-modified zeolite tested was also moderately effective and efficient for removing atrazine. Regardless of the initial atrazine concentration and batch test duration time, the SMZeo filter material removed on average between 43.8% to 59.9% of the atrazine based on immunoassay measurements or between 71.5% to 82.8% of the atrazine based on GC-MS measurements. (The 82.8% average atrazine decrease obtained with GC-MS measurements was for the moderate-concentration, 4 h test set, and as previously discussed, GC-MS atrazine measurements for

moderate-concentration, 4 h test may be of questionable validity.) Table 3a shows that the percent atrazine removal remained about the same for the moderate, high, and extreme concentration solutions, while table 4a indicates that the amount of atrazine removed by SMZeo is time dependent to a certain extent (chemical non-equilibrium) because as test duration increases so too does atrazine removal.

The interlayer of the surfactant bilayer is comprised of the hydrophobic hydrocarbon chain portions of the surfactant molecules (fig. 1). This hydrophobic interlayer in turn provides a medium in which organic compounds, such as atrazine, can be partitioned out of the aqueous solution via hydrophobic interactions (Bowman, 2003). Although somewhat less likely, some chloro-organic pesticides, such as atrazine, are moderately polar (Bohn et al., 1985; King et al., 1996) and could therefore potentially be adsorbed at negatively charged zeolite surfaces not covered with surfactant or at the surfactant/water interface in locations where surfactant bilayers cover the zeolite surfaces.

GENERAL COMMENTS

None of the five filter materials tested proved individually to be completely effective and efficient in removing all three nutrient and pesticide contaminants. Therefore, where effective and efficient removal of mixed nutrient/pesticide contaminants is required, more than one filter material may be needed. Employing more than one filter material may involve mixing the materials together, assuming there are no compatibility issues, or alternatively, installing the materials in a series of separate compartments within the filter treatment system. However, before field pilot tests of large or small scale filter treatment system are initiated, more laboratory investigation of potential filter materials is necessary, especially hydraulic conductivity measurements, flow cell experiments, and other tests for determination of physical and chemical properties.

SUMMARY AND CONCLUSIONS

A laboratory batch test study was conducted to evaluate the effectiveness and efficiency of five filter materials for removing mixed nutrient/pesticide contaminants (nitrate, phosphate, and atrazine) from subsurface drainage waters. The five filter materials tested included a steam activated carbon, a high calcium oxide-high carbon fly ash, an iron sulfide, a sulfur-modified iron, and a surfactant-modified zeolite. Effectiveness was tested against initial contaminant solution concentrations that varied from 10 to 50 to 200 mg L^{-1} for nitrate-nitrogen, from 0.1 to 0.25 to 1.0 mg L^{-1} for phosphate-phosphorus, and from 0.1 to 0.4 to 0.5 mg L^{-1} for atrazine, while efficiency was evaluated with respect to exposure time by varying test durations from 24 to 4 to 1 h. For each batch test, 5 g of a particular filter material were mixed in a Teflon centrifuge with 40 g of solution (38 g of solution in the case of tests with the steam activated carbon). Mixing of the filter material and solution within the Teflon centrifuge tube was accomplished with a laboratory rotator operated at 20 rpm. There were seven batch test replicates for each filter material, solution concentration, and test duration combination. Six replicate control batch tests without filter material were performed for each solution concentration and

test duration combination. The major findings of this research are listed as follows:

- All five filter materials removed measurable amounts of nitrate (NO_3^-), phosphate (PO_4^{3-}), and/or atrazine; however, for a particular contaminant, at least one or two of the filter materials were found to work better than the others.
- Sulfur-modified iron proved the most effective and efficient for treating NO_3^- , based on reductions greater than 95% across the range of initial concentration levels and exposure times.
- Surfactant-modified zeolite and the high calcium oxide-high carbon fly had the greatest effectiveness and efficiency for removal of PO_4^{3-} (50% or more for all three initial concentration levels and all three test durations).
- For atrazine, the most promising results with respect to effectiveness/efficiency were obtained with the steam activated carbon and the high calcium oxide-high carbon fly ash, which removed almost 100% of this particular pesticide regardless of initial concentration level and exposure time.
- Overall, there seem to be several filter materials having potential to remove substantial amounts of at least one nutrient/pesticide contaminant from subsurface drainage water. The effective and efficient removal of combined NO_3^- , PO_4^{3-} , and pesticide (such as atrazine) contaminants from drainage water will likely require a filter treatment system than contains at least two different filter materials.

Results of this investigation could eventually be applied to technology that targets farm operators, golf course superintendents, municipal managers, etc., who at present or in the near future may have responsibility for preventing excessive off-site release of nutrients and pesticides from subsurface drainage systems into local waterways. However, further research, including additional laboratory experiments, economic analysis, and finally, field pilot tests, is needed to determine if any of the five filter materials evaluated in this study have feasibility alone or in combination for widespread use in removing mixed nutrient/pesticide contaminants from subsurface drainage waters within both small- and large-scale settings.

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